

SUPPORTING INFORMATION

Alkylaluminum-Complexed Zirconocene Hydrides – Identification of Hydride-Bridged Species by NMR-Spectroscopy.

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Figure S1. ^1H spectrum of $(\text{C}_5\text{H}_5)_2\text{ZrH}_2$ (**3**) with 1 equiv. HAl^iBu_2 and 1 equiv. ClAl^iBu_2 in benzene- d_6 at 25°C .

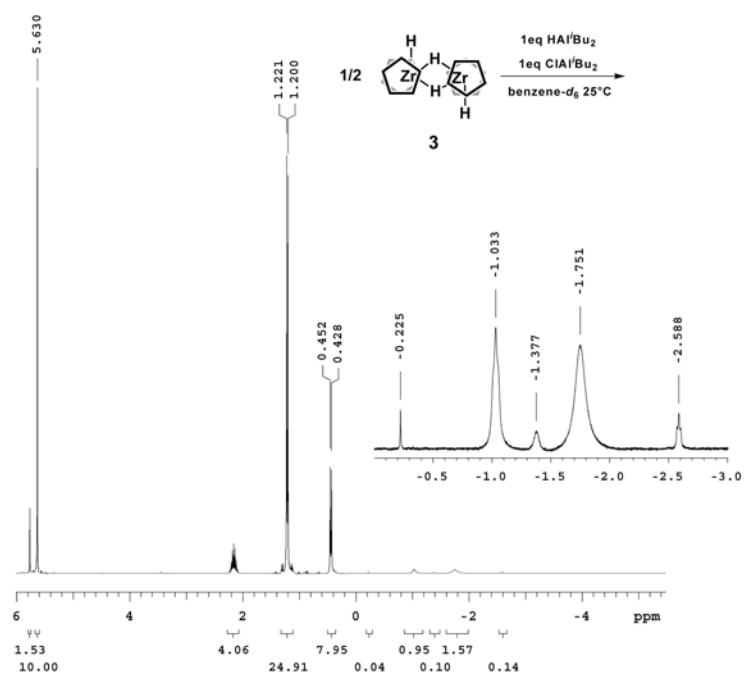


Figure S2. ^1H spectrum of $(\text{C}_5\text{H}_5)_2\text{ZrH}_2$ (**3**) with 1 equiv. HAl^iBu_2 and 2 equiv. ClAl^iBu_2 in benzene- d_6 at 25°C .

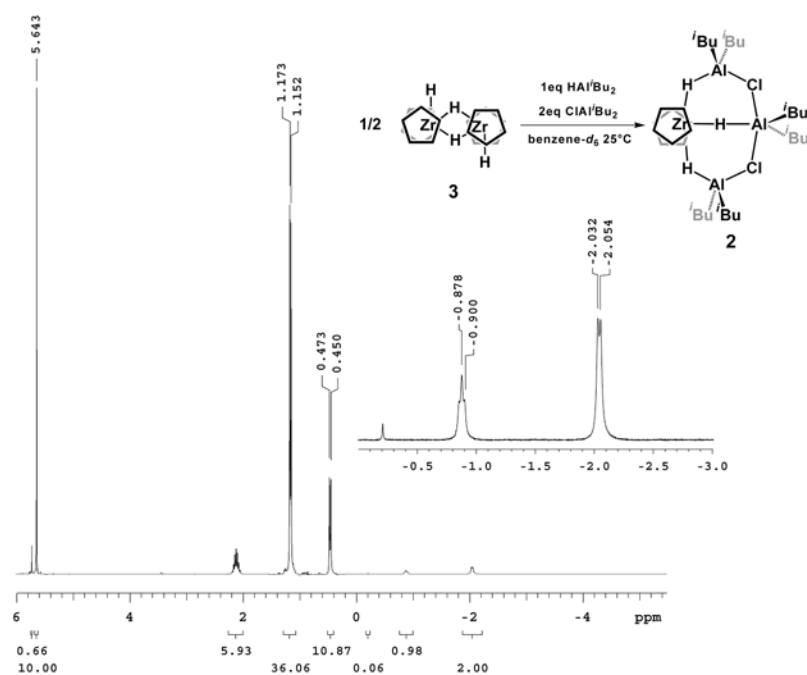


Figure S3. ^1H spectrum of $(\text{C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)_3(\mu\text{-H})_3$ in toluene- d_8 at -60°C .

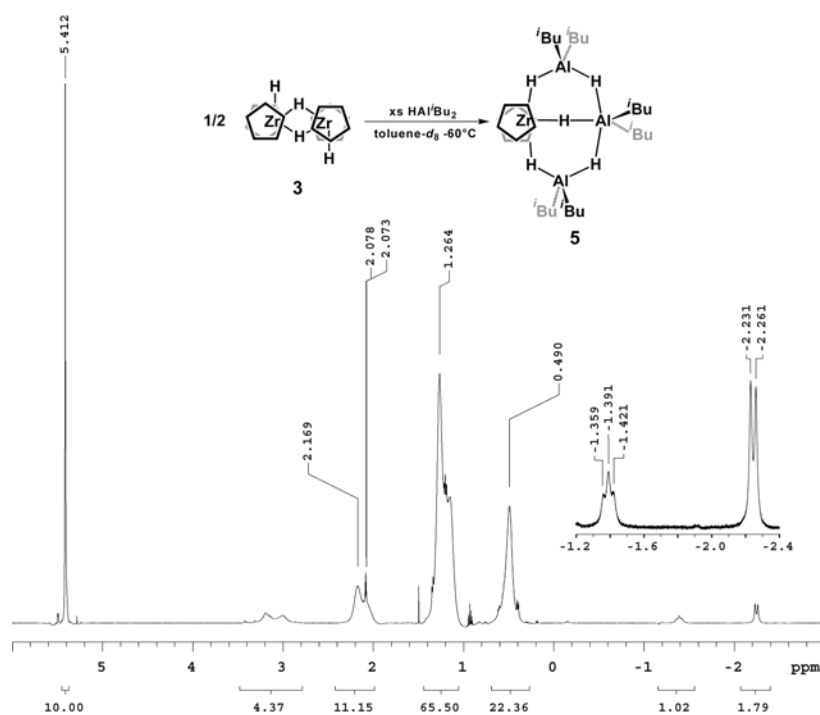


Figure S4. ^1H spectrum of $(^n\text{Bu-Cp})_2\text{ZrCl}_2$ (6) with 3 equiv. HAl^iBu_2 in benzene- d_6 at 25°C .

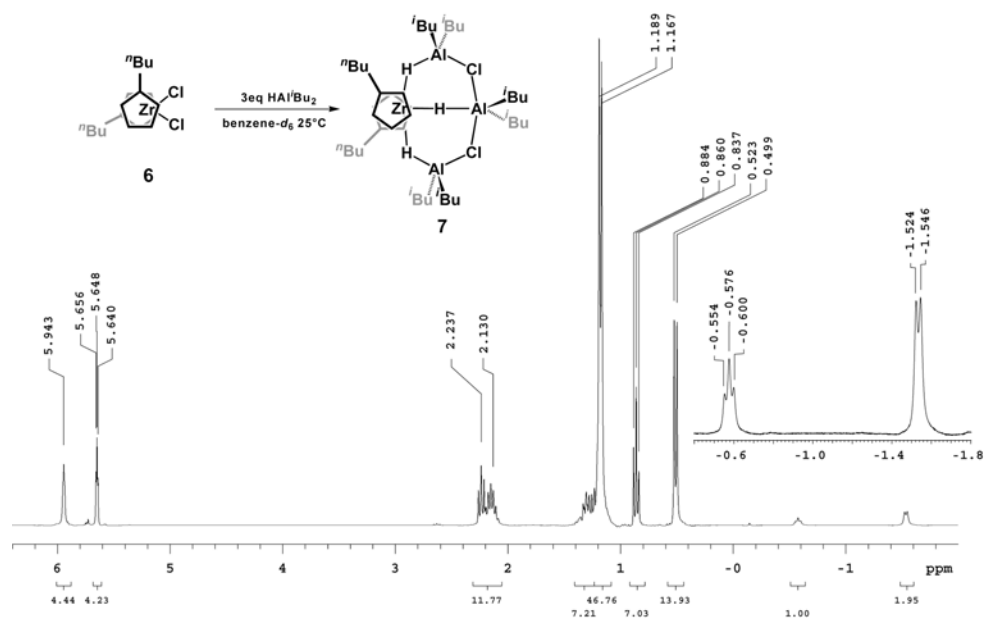


Figure S5. ^1H spectrum of $(1,2\text{-Me}_2\text{-C}_3\text{H}_3)_2\text{ZrCl}_2$ (**8**) with excess HAl^iBu_2 in benzene- d_6 at 25°C .

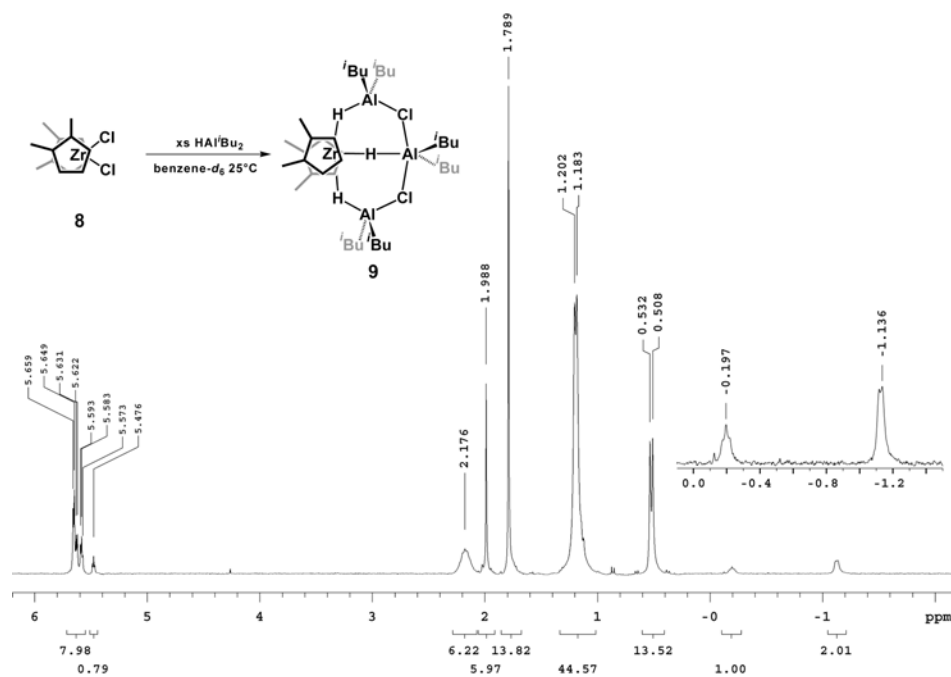


Figure S6. ^1H spectrum of $(\text{Me}_3\text{Si-C}_5\text{H}_4)_2\text{ZrCl}_2$ (**10**) with 2 equiv. HAl^iBu_2 in toluene- d_8 at -75°C .

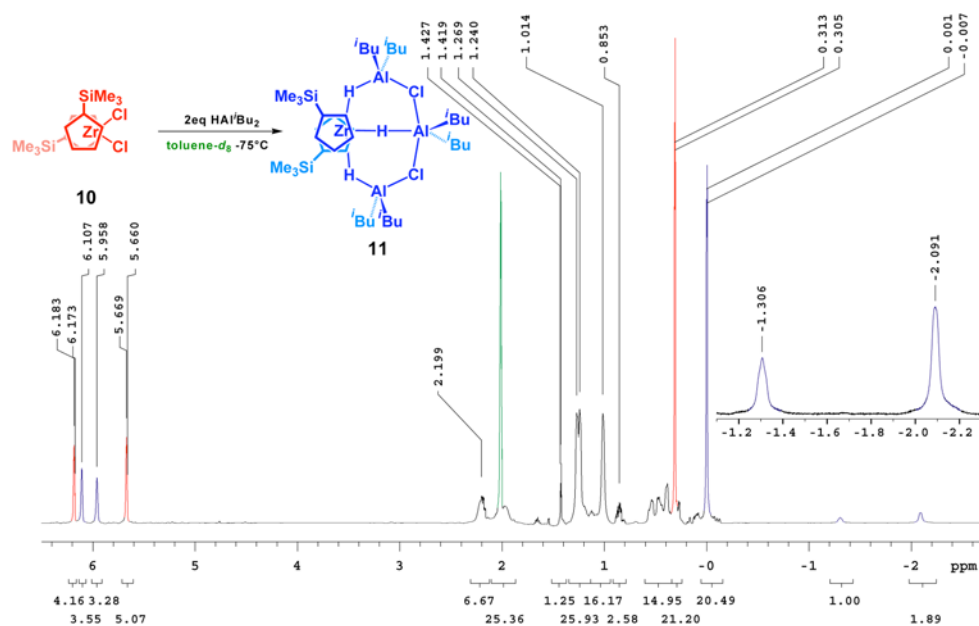


Figure S7. ^1H spectrum of $(\text{C}_5\text{Me}_5)_2\text{ZrH}_2$ (**13**) with 2 equiv. Al^iBu_3 to give $(\text{C}_5\text{Me}_5)_2\text{ZrH}^i\text{Bu}$ (**14**) and $(\text{C}_5\text{Me}_5)_2\text{Zr}^i\text{Bu}_2$ (**15**) in benzene- d_6 at 25°C .

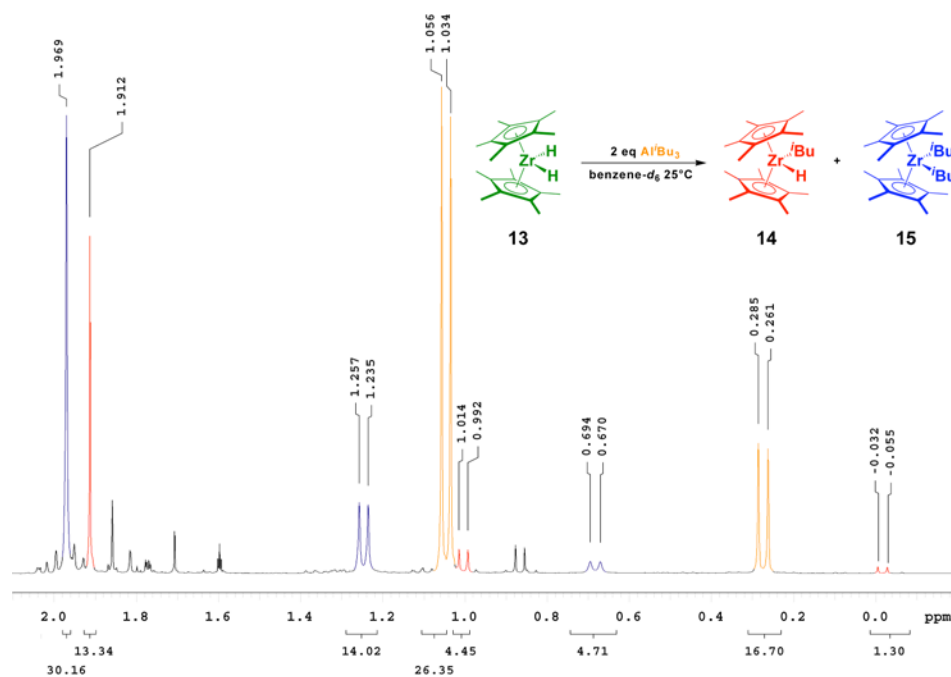


Figure S8. ^1H spectrum of $(\text{EBI})\text{ZrCl}_2$ (**17**) with 2 equiv. HA^iBu_2 in benzene- d_6 at 25°C .

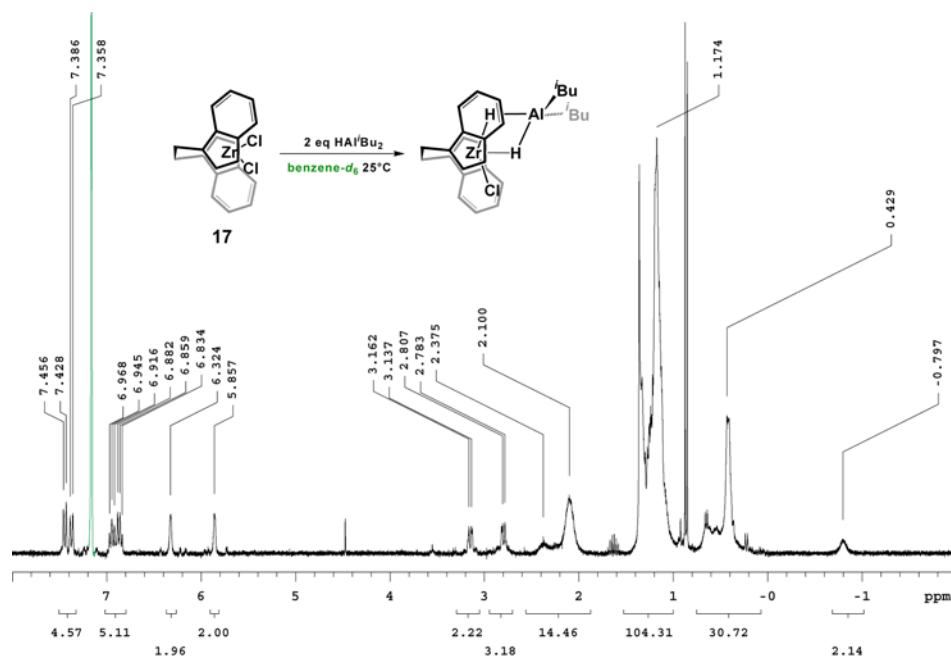


Figure S9. (EBTHI)ZrCl₂ (**18**) with 2 equiv. HAl^{*i*}Bu₂ in benzene-*d*₆ at 25°C.

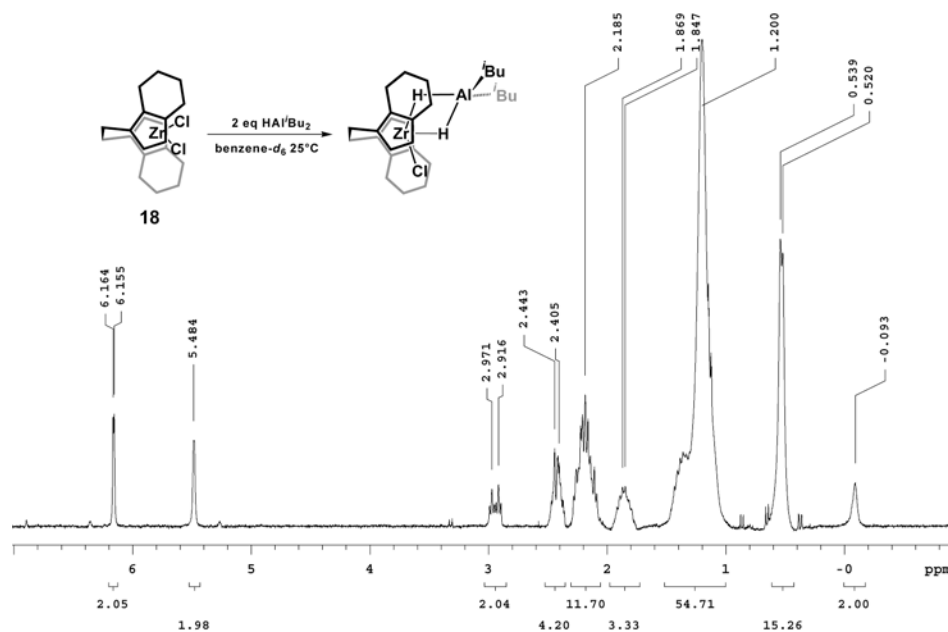


Figure S10. ¹H spectrum of Me₂C(C₅H₄)₂ZrCl₂ (**19**) with excess HAl^{*i*}Bu₂ in benzene-*d*₆ at 25°C.

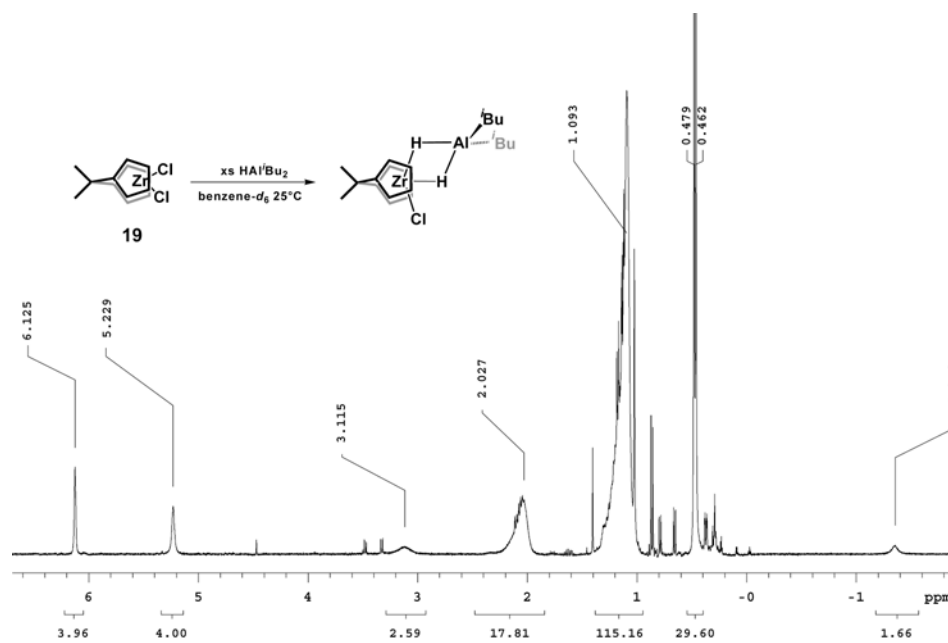


Figure S11. ^1H spectrum of $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (**19**) with 6 equiv. HAl^iBu_2 in benzene- d_6 at 25°C .

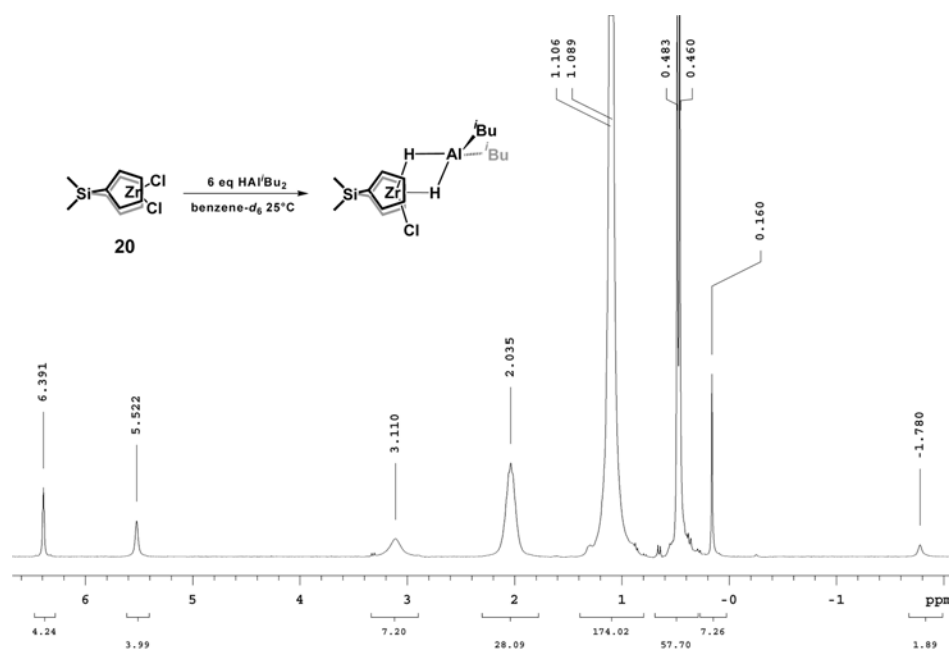


Figure S12. ^1H spectrum of $\text{Me}_2\text{Si}(2,4\text{-Me}_2\text{-C}_5\text{H}_2)_2\text{ZrCl}_2$ (**21**) with excess HAl^iBu_2 in benzene- d_6 at 25°C .

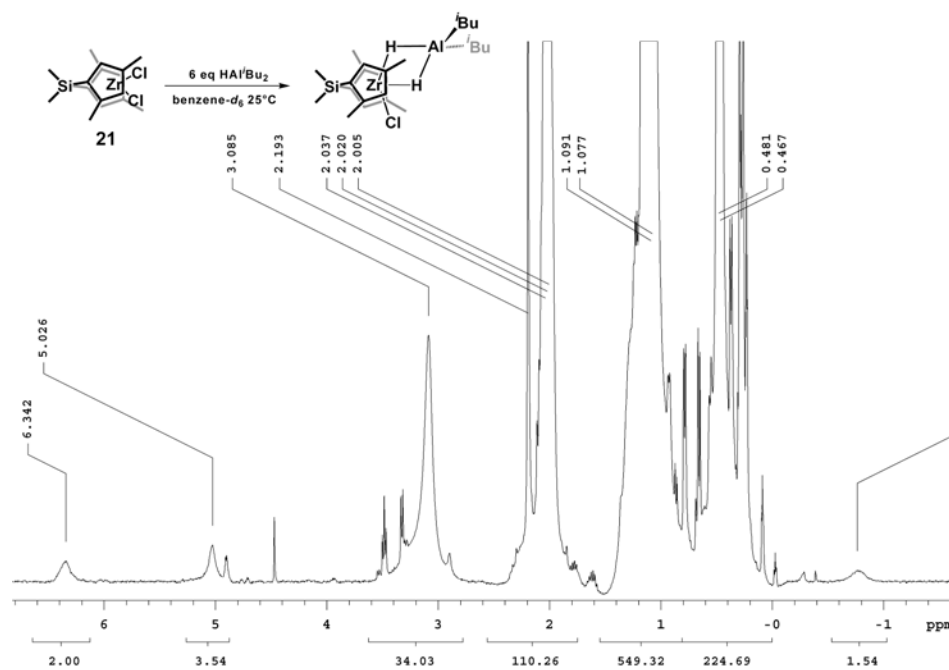


Figure S13. ^1H spectrum of $(\text{Me}_2\text{Si})_2(\text{C}_5\text{H}_3)_2\text{ZrCl}_2$ (**22**) with 2 equiv. HAl^iBu_2 in toluene- d_8 at -75°C .

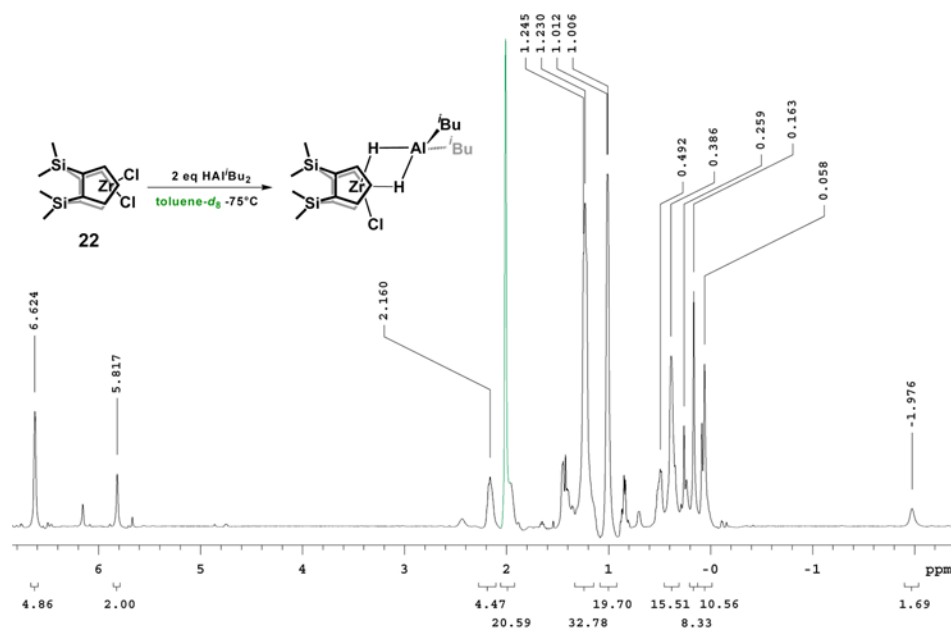


Figure S14. ^1H spectrum of $(\text{Me}_2\text{Si})_2(2,4\text{-}^i\text{Pr}_2\text{-C}_5\text{H}_3)_2\text{ZrCl}_2$ (**23**) with 2 equiv. HAl^iBu_2 in toluene- d_8 at -75°C .

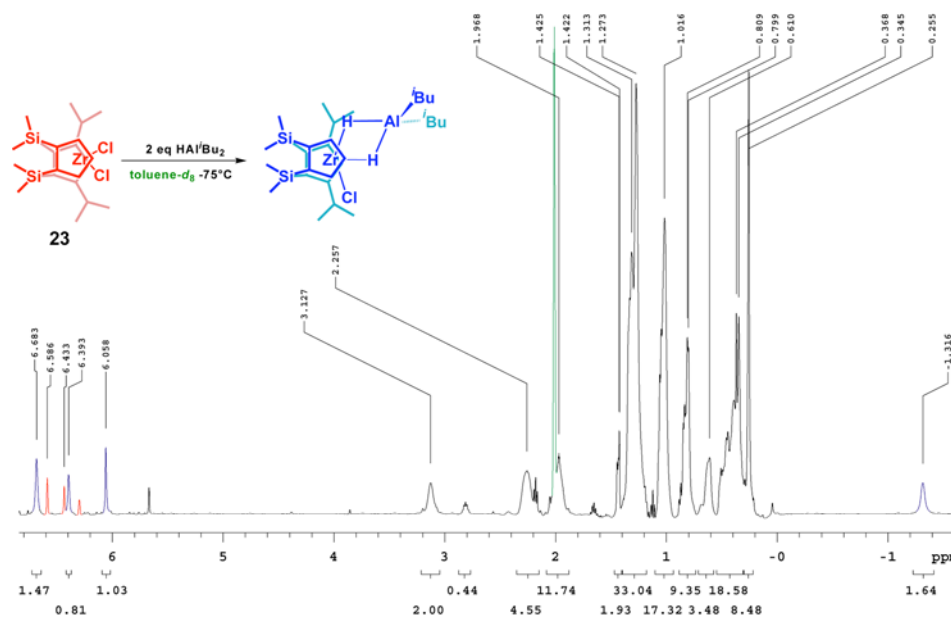


Figure S15. gCOSY of (EBTHI)ZrH(μ -H) $_2$ Al^{*i*}Bu₂ (**25**) in toluene-*d*₈ at -75°C.

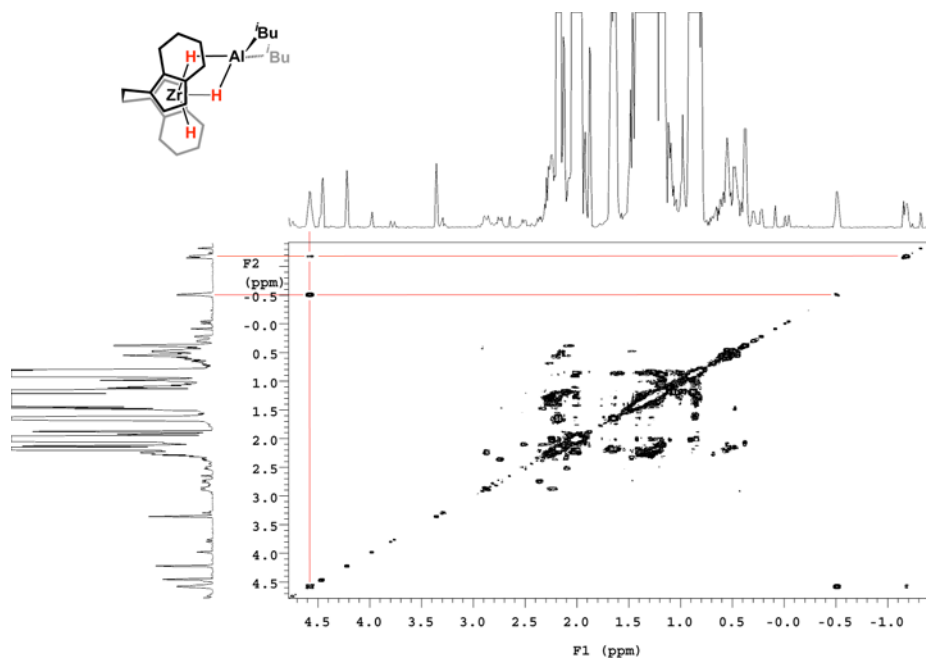


Figure S16. ¹H spectrum of ((EBTHI)ZrH(μ -H))₂ (**24**) with 4 equiv. HAl^{*i*}Bu₂ and 2 equiv. ClAl^{*i*}Bu₂ in benzene-*d*₆ at 25°C.

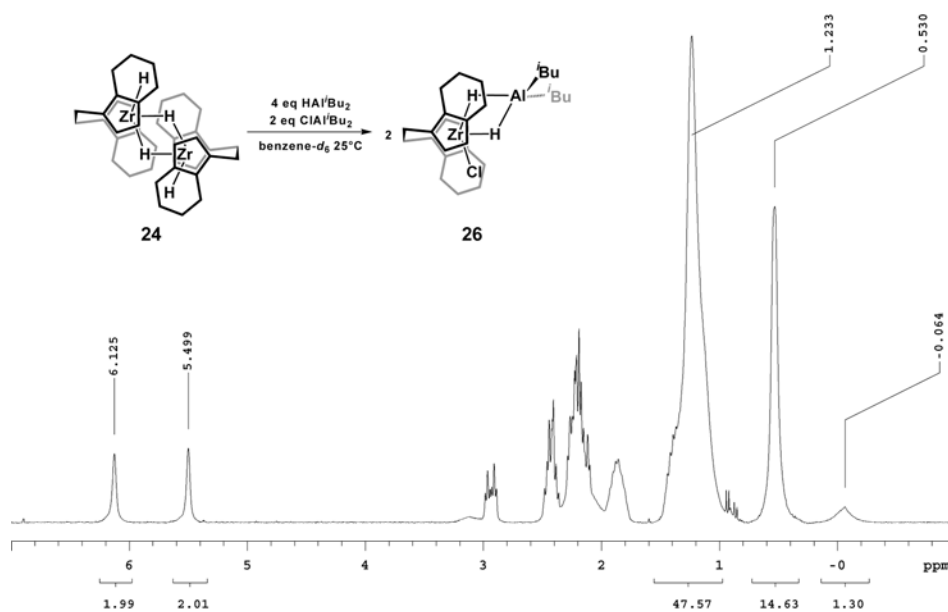


Figure S17. ^1H spectrum of $((\text{EBTHI})\text{ZrH}(\mu\text{-H})_2)$ (**24**) with 4 equiv. HAl^iBu_2 and 4 equiv. ClAl^iBu_2 in benzene- d_6 at 25°C.

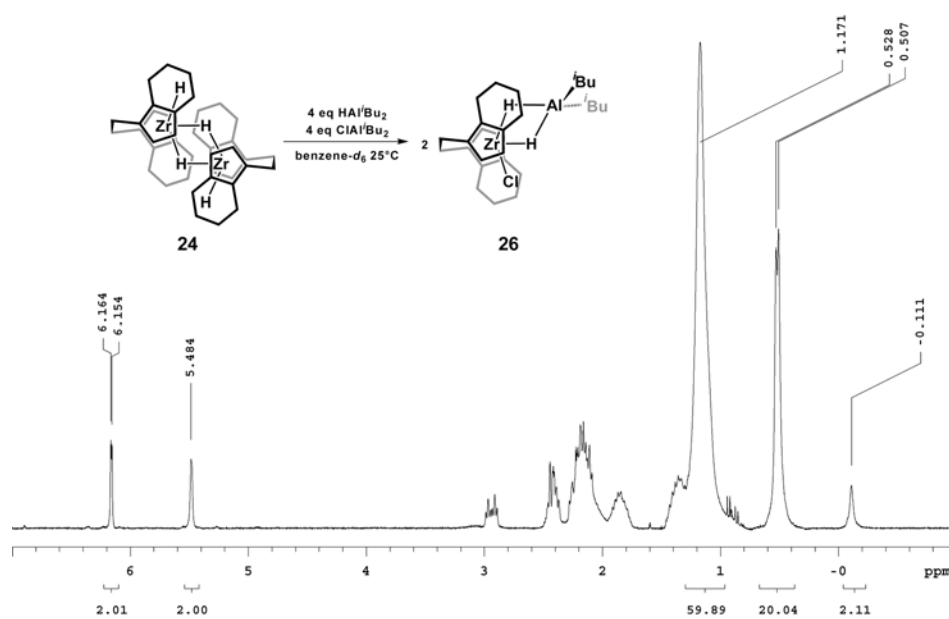


Figure S18. ^1H spectrum of $\text{rac-Me}_2\text{C}(\text{indenyl})_2\text{ZrCl}_2$ (**27**) with 2 equiv. HAl^iBu_2 in benzene- d_6 at 25°C.

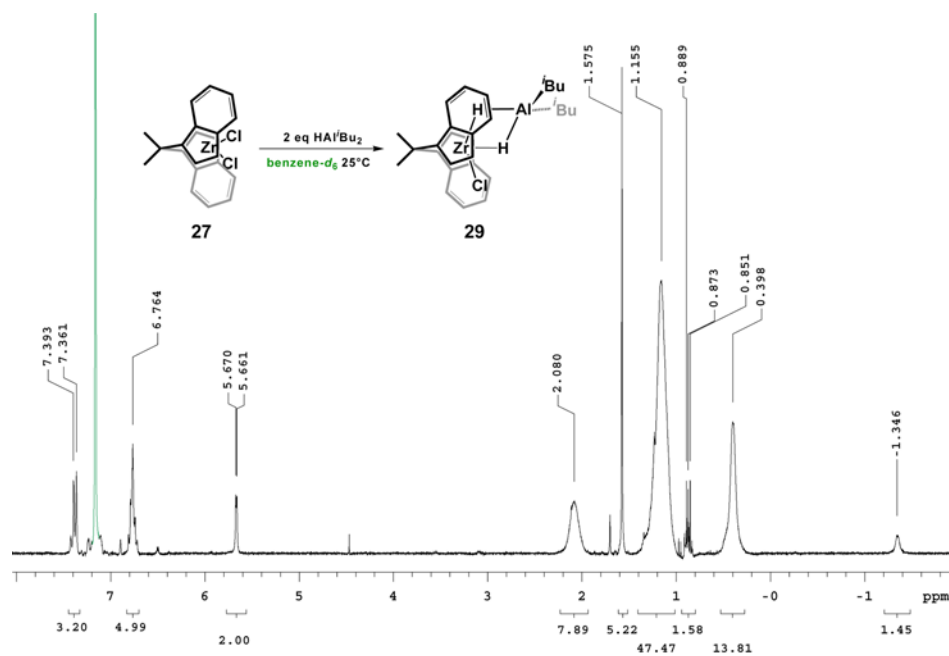


Figure S19. ^1H spectrum of *meso*- $\text{Me}_2\text{C}(\text{indenyl})_2\text{ZrCl}_2$ (**28**) with 2 equiv. HAl^iBu_2 in benzene- d_6 at 25°C .

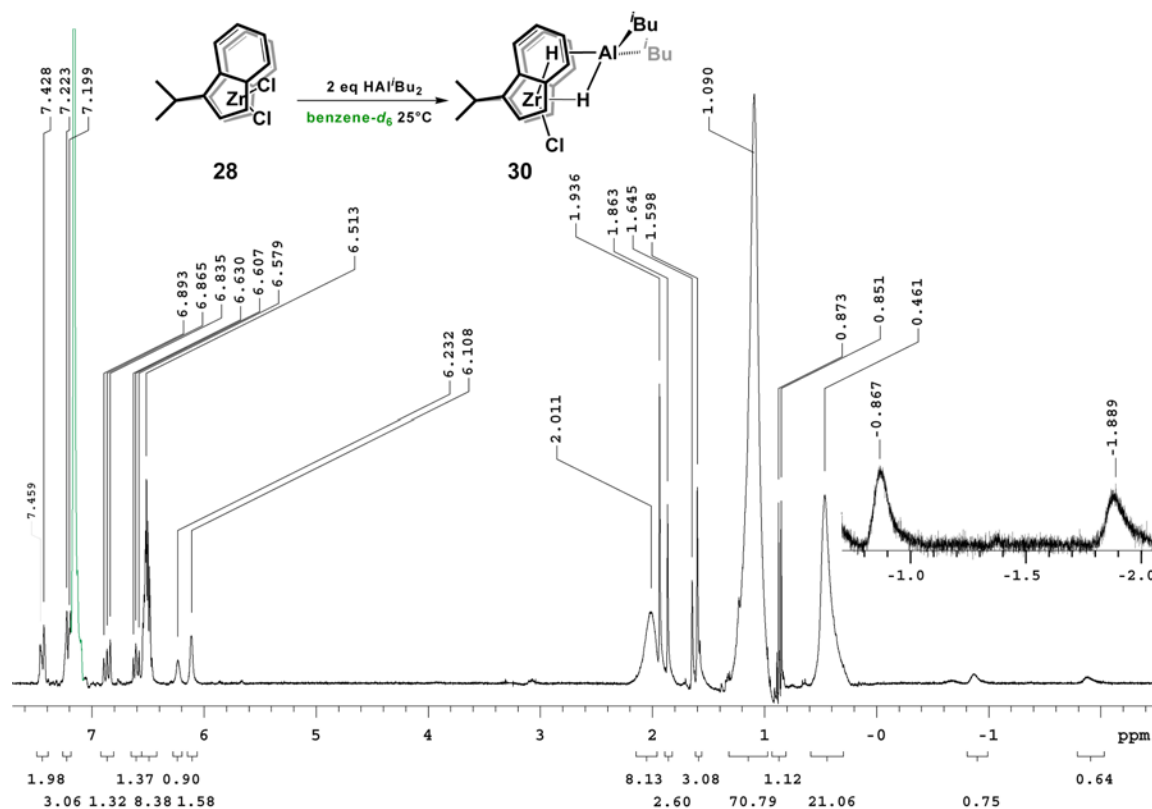


Figure S20. gCOSY of *rac*- $\text{Me}_2\text{Si}((2\text{-Me}_3\text{Si-4-Me}_3\text{C-C}_5\text{H}_2)\text{ZrH}(\mu\text{-H})_2\text{Al}^i\text{Bu}_2)$ (**32**) in toluene- d_8 at -75°C

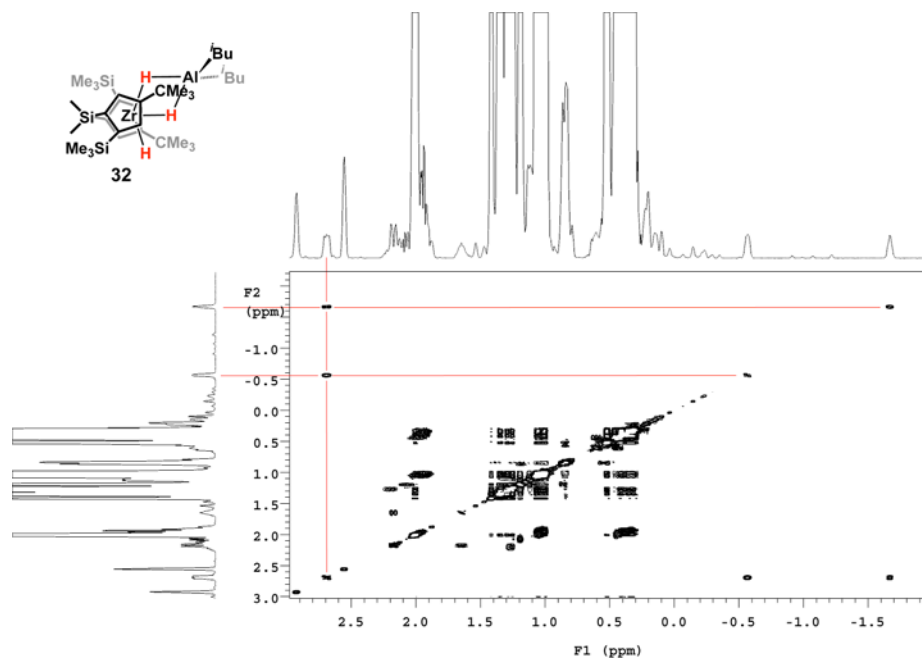


Figure S21. noedif of **32** in benzene- d_6 at 25°C irradiating the central hydride resonance (**A**) and the terminal unbridged hydride resonance (**B**).

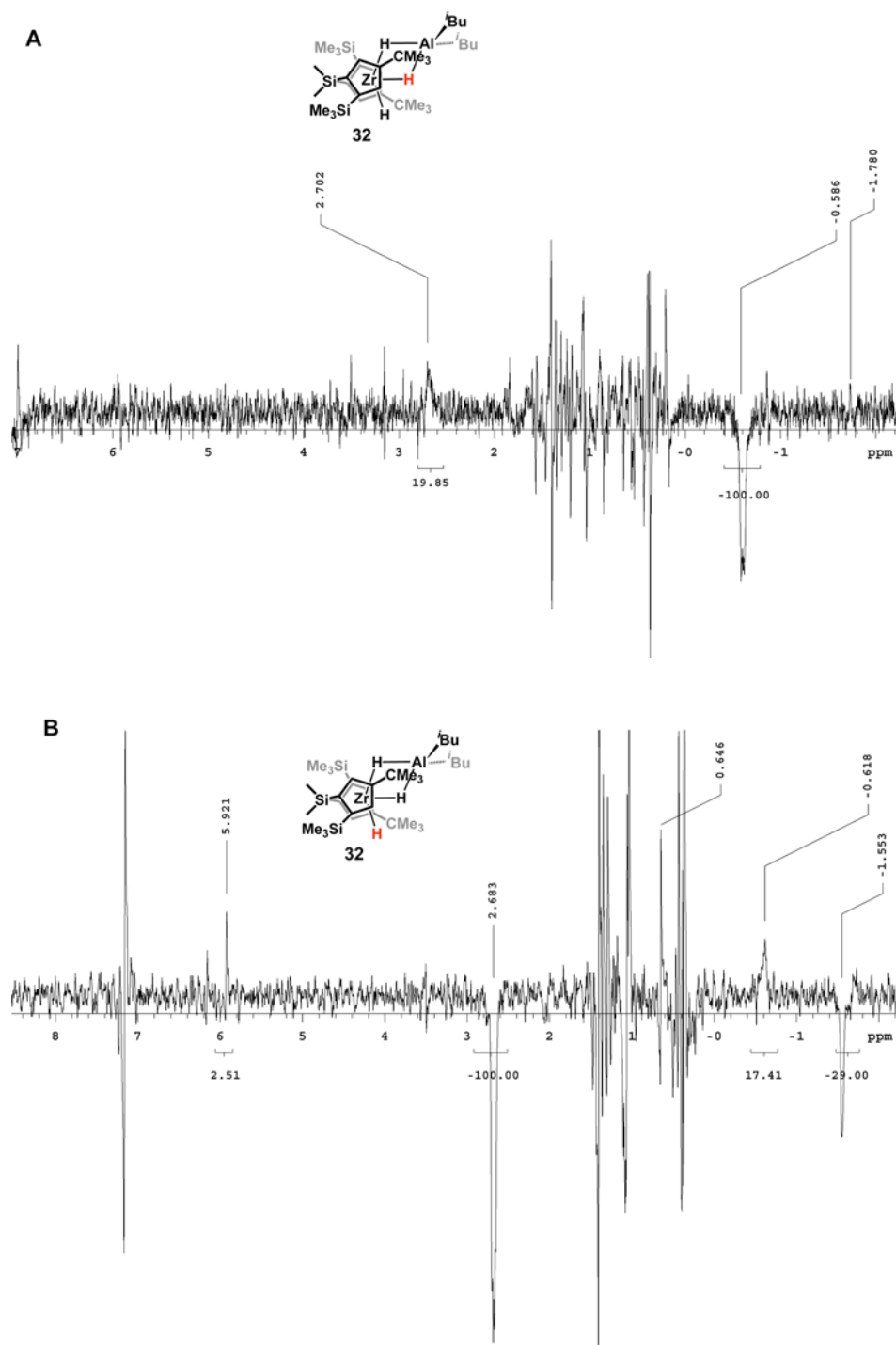


Figure S22. ^1H spectrum of *meso*- $\text{Me}_2\text{Si}(3\text{-Me}_3\text{C-C}_5\text{H}_3)_2\text{ZrCl}_2$ (**33**) with 2 equiv. HAl^iBu_2 in $\text{toluene-}d_8$ at 25°C .

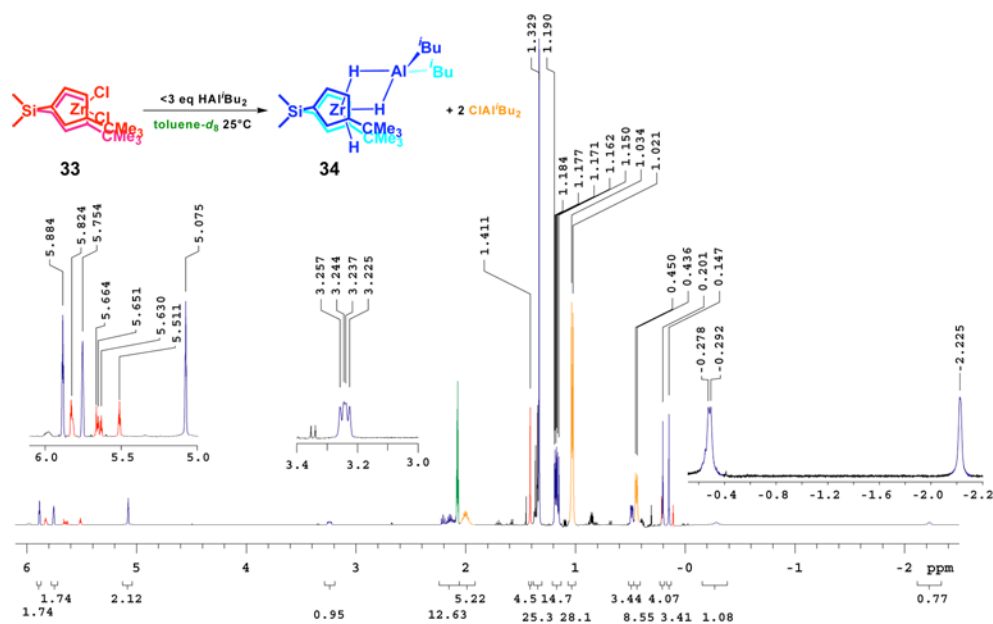


Figure S23. gCOSY of **33** with 2 equiv. HAl^iBu_2 in $\text{toluene-}d_8$ at 25°C .

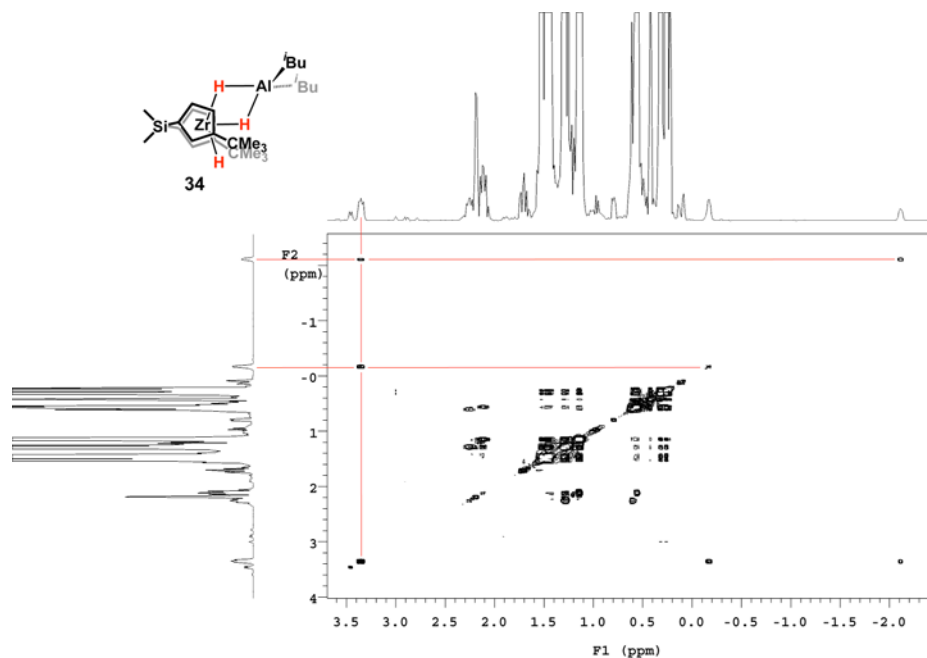


Figure S24. noedif of **33** with 3 equiv. HAl^iBu_2 in benzene- d_6 at 25°C.

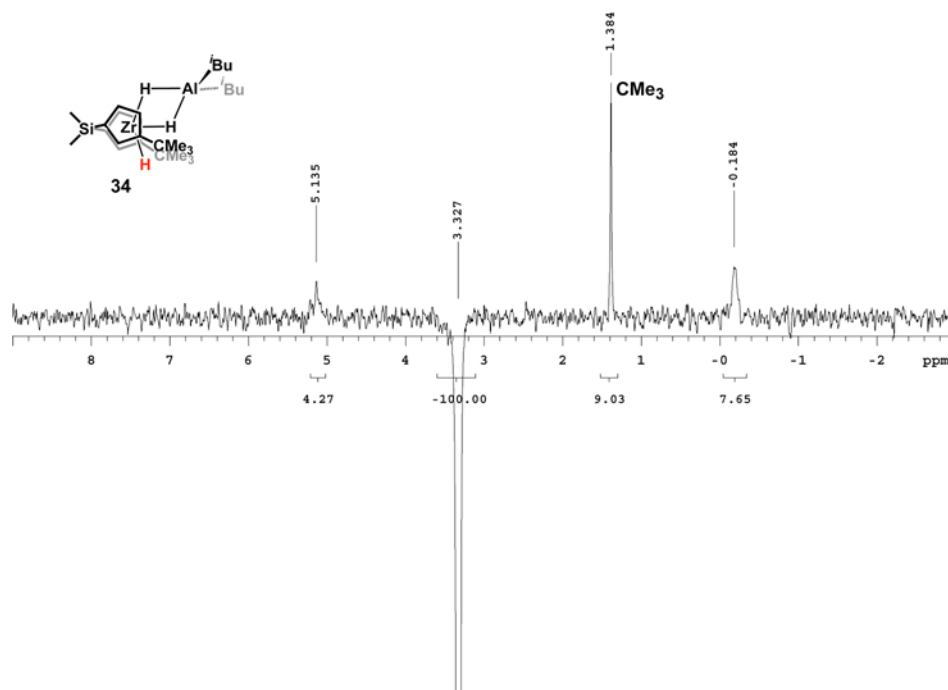


Figure S25. ^1H spectrum of $\text{H}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (**35**) with 4 equiv. HAl^iBu_2 in toluene- d_8 at 0°C.

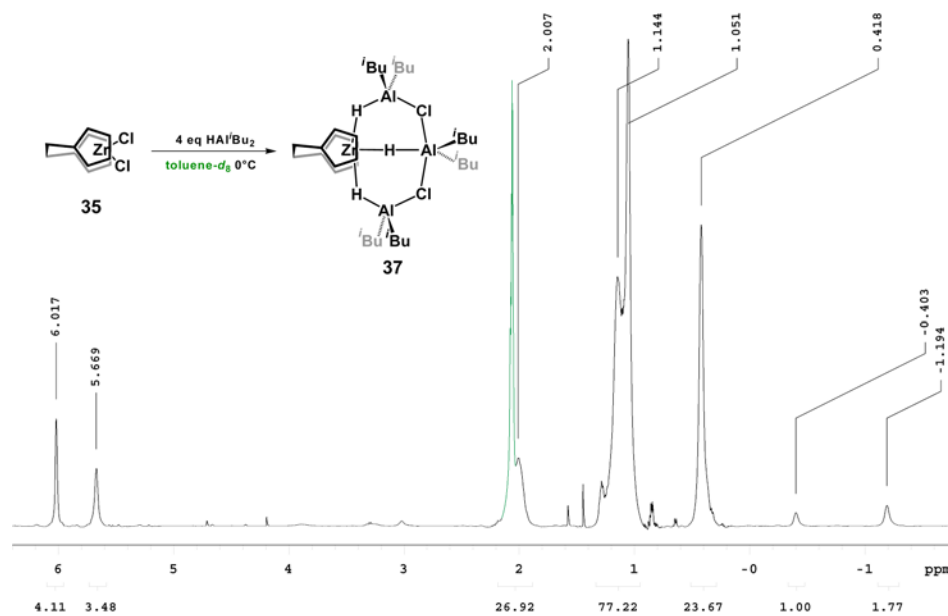


Figure S26. NOESY1D of $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (**36**) with 4 equiv. HAl^iBu_2 in benzene- d_6 at 25°C.

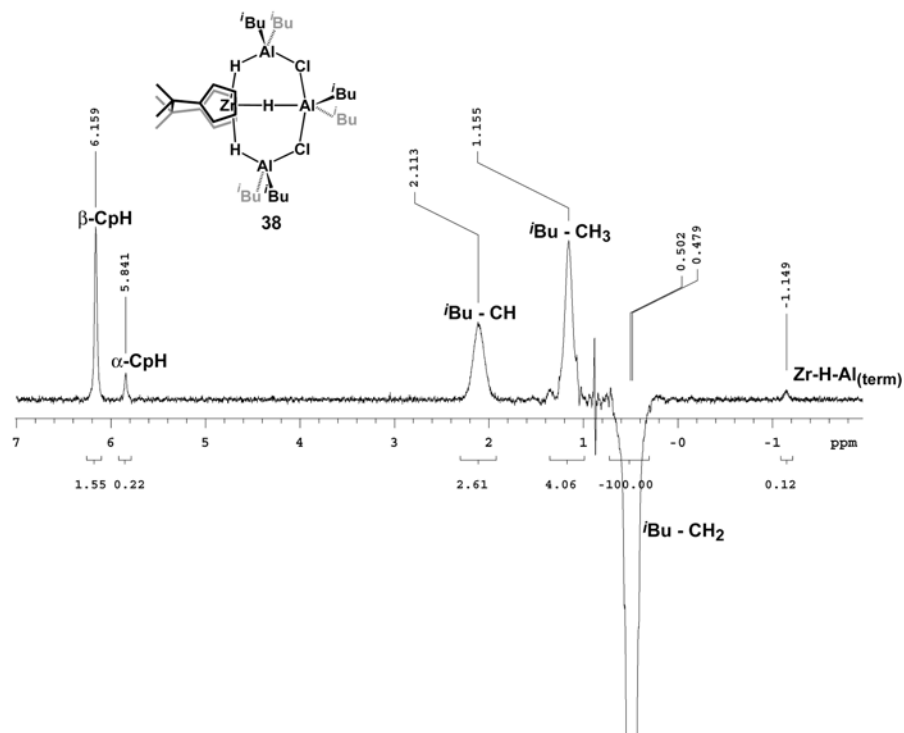
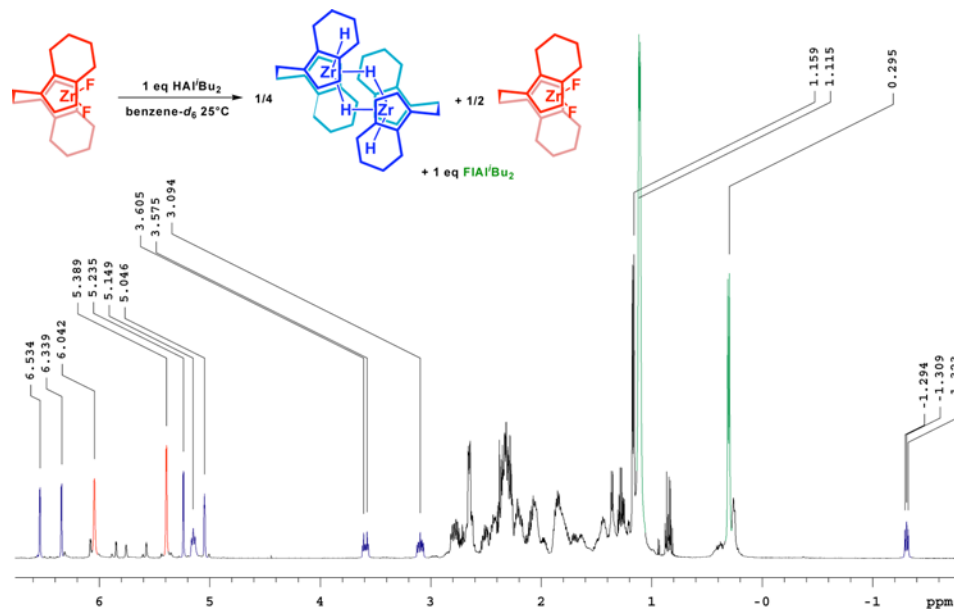


Figure S27. ^1H spectrum of $(\text{EBTHI})\text{ZrF}_2$ with 1 equiv. HAl^iBu_2 in benzene- d_6 at 25°C.



Appendix S-1. Analysis of changes in the chemical shift of the ZrH_2 signal of $(\text{SBI})\text{ZrCl}(\mu\text{-H})_2\text{Al}^i\text{Bu}_2$ upon addition of Al_2Me_6 .

1) Adduct Formation:

Adduct formation of $(\text{SBI})\text{ZrCl}(\mu\text{-H})_2\text{Al}^i\text{Bu}_2$ with Al_2Me_6 , is represented by Equ. 1, with **A** representing the starting complex, **X₂** the AlMe_3 dimer and **AX** the adduct:



The equilibrium constant K for this reaction is represented by Equ. 2:

$$K = \frac{[AX]}{[A]\sqrt{[X_2]}} \quad (2)$$

Under conditions of rapid exchange between **A** and **AX** the chemical shift of the resulting signal, δ , is the weighted average of the chemical shifts of **A**, δ_A , and **AX**, δ_{AX} (Equ. 3).

$$\delta = \frac{[A]}{[AX] + [A]} \delta_A + \frac{[AX]}{[AX] + [A]} \delta_{AX} \quad (3)$$

The difference in chemical shift, $\Delta\delta$, of the signal at any given concentration of added **X**, δ , and that of pure **A** is given by Equ. 4.

$$\Delta\delta = \delta - \delta_A \quad (4)$$

Combining Equ. 3 and Equ. 4 we get:

$$\Delta\delta = \left(\frac{[A]}{[AX] + [A]} - 1 \right) \delta_A + \frac{[AX]}{[AX] + [A]} \delta_{AX} \quad (5)$$

Which simplifies to:

$$\Delta\delta = \frac{[AX]}{[AX] + [A]} (\delta_{AX} - \delta_A) \quad (6)$$

With the maximum change in chemical shift represented as $\Delta\delta_{\text{max}}$, we get Equ. 7.

$$\Delta\delta_{\text{max}} = \delta_{AX} - \delta_A \quad (7)$$

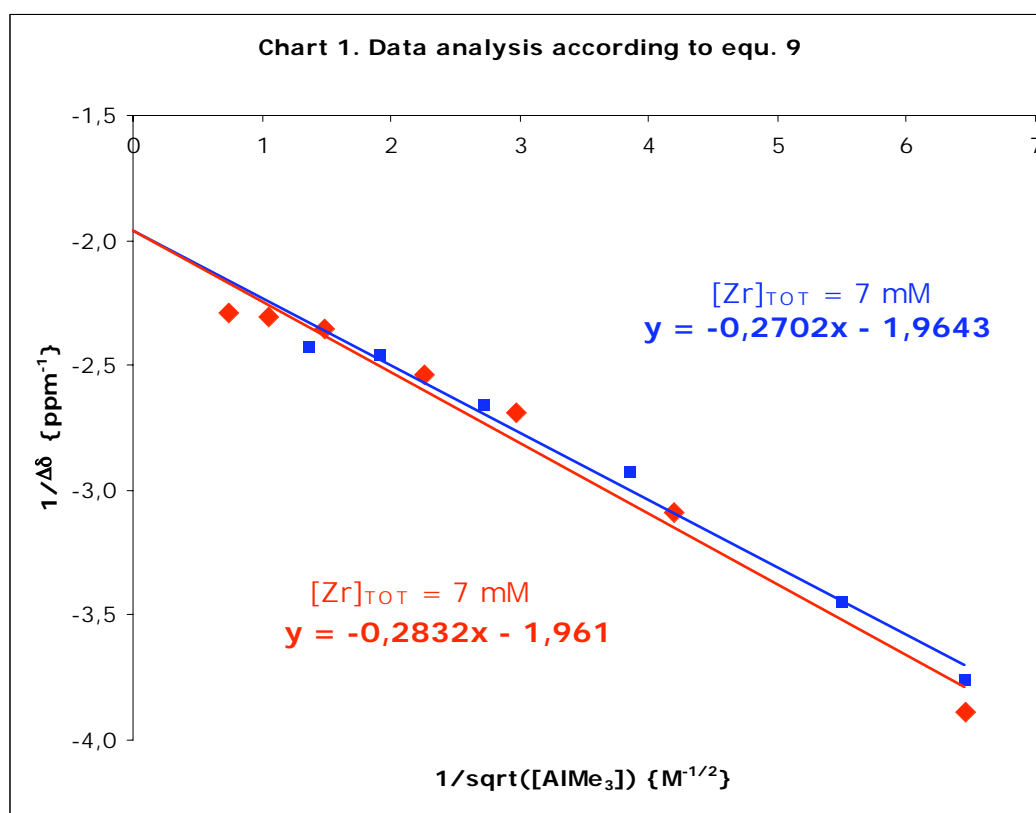
Taking the reciprocal of Equ. 6 and using Equ. 7 gives Equ. 8:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\text{max}}} + \frac{1}{\Delta\delta_{\text{max}}} \cdot \frac{[A]}{[AX]} \quad (8)$$

Together with the equilibrium constant, Equ. 2, this yields a Benesi-Hildebrand type relation (Equ. 9):

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max} K \sqrt{[X_2]}} \quad (9)$$

Assuming that K is small, the amount of X_2 added is approximately equal to the amount of X_2 in solution. A plot of the reciprocal of the change in chemical shift against the reciprocal of the square root of the concentration of Al_2Me_6 added should thus be linear, with a slope of $1/K$ and a y-axis intercept of $1/\delta_{AX}$, neither of which should depend on $[Zr]_{TOT}$.



The data plotted in Chart 1 according to Equation 9 approximate this requirement. Some curvature of the data in Chart 1 might originate from a partial dissociation of Al_2Me_6 to $AlMe_3$ in dilute solutions and/or from the fact that the most concentrated solutions of Al_2Me_6 contain up to 20 volume percent Al_2Me_6 , such that these solution can no longer be considered to be ideal solutions of Al_2Me_6 in benzene. Nevertheless, the values of $1/\delta_{\max}$ and of $1/K$ derived from the data for $[Zr] = 7$ mM and from those for $[Zr] = 28$ mM are indistinguishable within their error

margins. Our data are thus compatible with the view that the change in chemical shift of the ZrH_2 signal upon addition of Al_2Me_6 to a solution of $(\text{SBI})\text{Zr}(\text{Cl})(\mu\text{-H})_2\text{Al}^i\text{Bu}_2$ is due to formation of an adduct, e.g. of the type $(\text{SBI})\text{Zr}(\text{Cl}\cdots\text{AlMe}_3)(\mu\text{-H})_2\text{AlR}_2$, with $\text{R} = ^i\text{Bu}$ and/or Me .

2) Exchange Reaction:

The reaction of $(\text{SBI})\text{ZrCl}(\mu\text{-H})_2\text{Al}^i\text{Bu}_2$ to exchange either the Zr-bound Cl or an Al-bound ^iBu with one of the methyl groups of Al_2Me_6 , to yield $\text{Al}_2\text{Me}_5\text{X}$ where $\text{X} = \text{Cl}$ or ^iBu , is represented by Equ. 10, with **A** representing the starting ZrClH_2 complex, **X₂** the AlMe_3 dimer, **B** the exchange product and **Y** the $\text{Al}_2\text{Me}_5\text{X}$ product:



The equilibrium constant K for this reaction is represented by Equ. 2:

$$K = \frac{[\text{B}][\text{Y}]}{[\text{A}][\text{X}_2]} \quad (11)$$

We can use the same derivation as for Equation 8, except $[\text{AX}]$ is now replaced by $[\text{B}]$.

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \cdot \frac{[\text{A}]}{[\text{B}]} \quad (12)$$

Using the equilibrium constant, Equ. 11, this yields a Benesi-Hildebrand type relation (Equ. 13):

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \cdot \frac{[\text{Y}]}{K[\text{X}_2]} \quad (13)$$

Since we are adding **X₂** to **A**, $[\text{Y}]$ is equal to $[\text{B}]$, yielding:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \cdot \frac{[\text{B}]}{K[\text{X}_2]} \quad (14)$$

Rearranging to give a $y = mx+b$ format gives:

$$\frac{1}{\Delta\delta} = \left(\frac{[\text{B}]}{\Delta\delta_{\max} K} \right) \cdot \frac{1}{[\text{X}_2]} + \frac{1}{\Delta\delta_{\max}} \quad (15)$$

Alternatively Equ. 14 can be modified by using the following relationship which is derived by combining Equ. 3, 4 and 7:

$$\Delta\delta = \Delta\delta_{\max} \frac{[\text{B}]}{[\text{A}] + [\text{B}]} \quad (16)$$

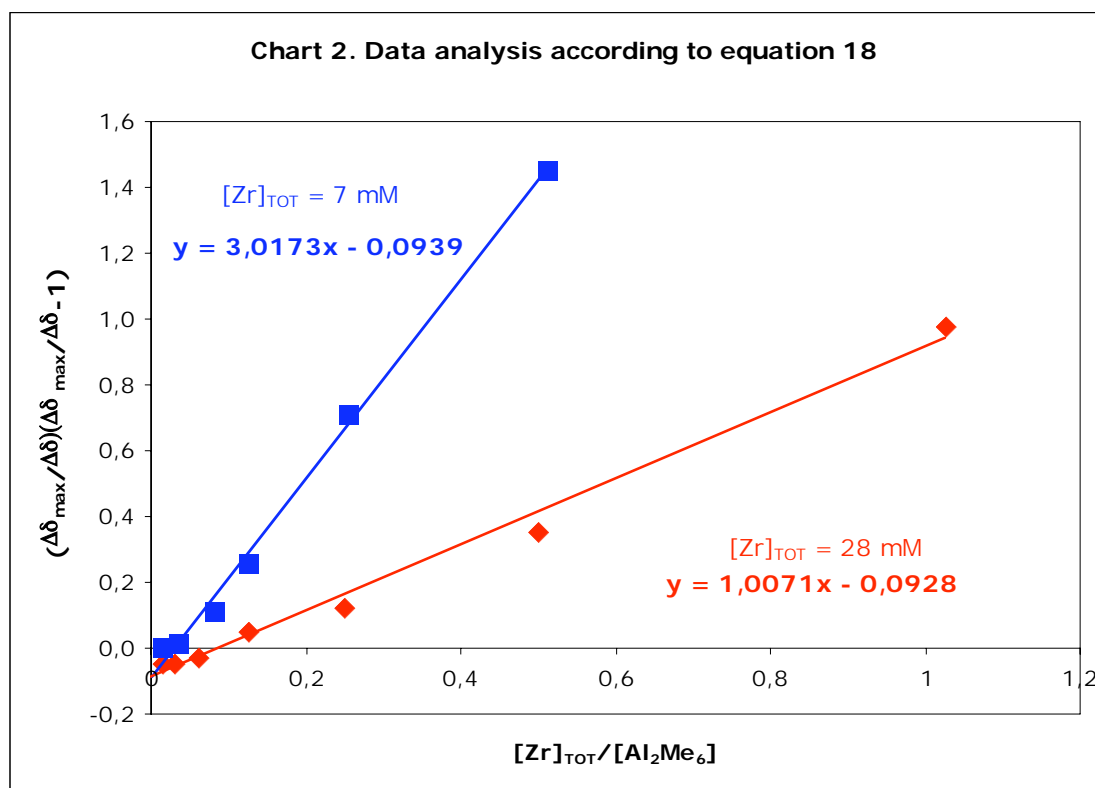
Solving for $[\text{B}]$ and substituting into Equation 14 gives:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{\Delta\delta}{\Delta\delta_{\max}} \cdot \frac{[A] + [B]}{\Delta\delta_{\max} K [X_2]} \quad (17)$$

With $[A] + [B] = [\text{Zr}]_{\text{TOT}}$ and $[X_2] = [\text{Al}_2\text{Me}_6]$, equation 17 can be rearranged to:

$$\left(\frac{\Delta\delta_{\max}}{\Delta\delta} - 1 \right) \frac{\Delta\delta_{\max}}{\Delta\delta} = \frac{[\text{Zr}]_{\text{TOT}}}{K \cdot [\text{Al}_2\text{Me}_6]} \quad (18)$$

The value of $\Delta\delta_{\max}$ can be estimated from the chemical shift at the highest concentrations of Al_2Me_6 or from the plot in Chart 1. Assuming that K is small, the amount of Al_2Me_6 added is approximately equal to the amount of Al_2Me_6 in solution. Therefore, a plot of the left side of Equ.18 against $[\text{Zr}]_{\text{TOT}}/[\text{Al}_2\text{Me}_6]$ should give a straight line going through the origin, with a slope of $1/K$, which should thus be independent of $[\text{Zr}]_{\text{TOT}}$.



Inspection of such a plot (Chart 2) shows that the data do not meet this requirement. Instead, the slope of the data for $[\text{Zr}]_{\text{tot}} = 7 \text{ mM}$ is about three times larger than that of the data for $[\text{Zr}]_{\text{tot}} = 28 \text{ mM}$. The change in chemical shift of the ZrH_2 signal upon addition of Al_2Me_6 to a solution of $(\text{SBI})\text{Zr}(\text{Cl})(\mu\text{-H})_2\text{Al}^i\text{Bu}_2$ can thus **not** be due to an exchange reaction, e.g. of the Cl against a Me ligand.